

Immobilized α -Iminocarboxamide Nickel (II) Complex as Catalyst for Ethylene Homo-/Co-Polymerization

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Introduction

Nickel complexes are attractive as catalysts for ethylene polymerization due to a high potential for controlling properties of produced polymer. Bazan *et al.* reported that the Ni complex bearing α -iminocarboxamide ligand catalyzed copolymerization of ethylene with polar-functionalized norbornene [1]. Polar monomers have a strong affinity to cationic center as active species of the olefin polymerization and readily cause the catalyst deactivation. Therefore, his discovery has been innovative in the academic and industrial research field.

To apply this Ni complex in the industrial process, it is necessary to control the morphology of the resulted polymer by immobilizing that on support materials.

In this study, we prepared the catalysts immobilizing α -iminocarboxamide Ni(II) complex on acid-treated montmorillonite as a support and evaluated their properties as catalysts.

Experimental

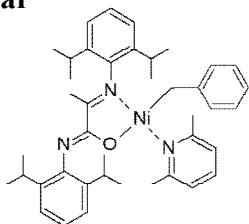


Fig. 1 structure of Ni complex **a**.

The α -iminocarboxamide Ni(II) complex **a** was synthesized according to the literature [1]. Acid-treated montmorillonite as a support was pretreated with triisobutylaluminum in toluene. Subsequently, the support was impregnated with a toluene solution of the complex **a**. The obtained solid was washed with toluene and dried *in vacuo* (**1a**). The slurry polymerization using **1a** was performed in hexane at 40 °C for 1h. During the polymerization, ethylene

was continuously fed at 0.7 MPa. Copolymerization of ethylene with 5-Norbornene-2-yl-acetate (NBA) using **1a** was carried out in the same conditions. Melting points of the obtained polymers were measured by DSC.

Result and discussion

The supported catalyst **1a** showed a moderate activity of 10 g-product g⁻¹-**1a** h⁻¹ during the ethylene homo-polymerization with excellent morphology of the product.

Melting point ($T_m=131^\circ\text{C}$) of polyethylene obtained by **1a** is much higher than that ($T_m=122^\circ\text{C}$) obtained by **a** in homogeneous polymerization under the same conditions. It suggested that the difference of the T_m was due to the number of branches produced by the chain-walking mechanism. Moreover, with addition of NBA, the catalyst **1a** did not promote the copolymerization, whereas the complex **a** produced ethylene/NBA copolymer in the presence of NBA.

The complex **a** isomerized from the N, O-bonding fashion to the N, N-bonding fashion which was inactive for the ethylene/NBA copolymerization [1]. Oxygen of the ligand might coordinate to Lewis acid sites located on the surface of montmorillonite, and nitrogen simultaneously coordinated to nickel center instead of oxygen. As the similar behavior, the coordination between a Lewis acid and oxygen of the α -iminocarboxamide Ni(II) complex have reported [2-3].

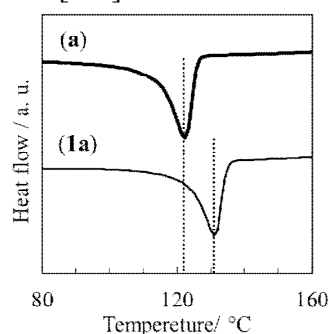


Fig 2 DSC patterns of polyethylene yielded by complex **a**, and supported catalyst **1a**.

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